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Low Energy Barrier Proton Transfer in Protonated Benzene−Water Complex

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Protonation of the rather weak πH-bonded benzene−water complex is studied at the MP2/6-31+G(d,p) computational level. It is shown that, contrary to the fact that benzene is more basic than water by 13.5 kcal/mol, the excess proton favors to reside on water forming the benzene−oxonium complex. This complex is formed via the coupled electron−proton transfer from the benzenium−water complex occurred through the low-energy barrier. The latter is associated with a transition state resembling a π-complex and resulting from an avoided crossing of the potential energy surfaces describing the dissociation channels of both benzenium−water and benzene−oxonium complexes, respectively.

1. Introduction

One of the most useful quantity in physical chemistry is the proton affinity (PA).[1] The proton affinity of a molecular system A, PA(A), is defined as the negative enthalpy of the reaction of protonation $A + H^+ \rightarrow AH^+$. An accuracy of the evaluation of PAs is often verified with water whose experimental PA(H_2O) = 166.5 ± 1 kcal/mol.[2] On the other hand, the most accurate theoretical estimation to date of PA(H_2O) performed at the CCSD(T)/aug-cc-pV5Z level comprises of 165.1 ± 0.3 kcal/mol.[3a] It has been recently shown[3b] that, depending on the computational level, the theoretical value of PA(H_2O) varies in the interval from 163.02 to 171.13 kcal/mol. The lower boundary is obtained at the G2 level whereas the upper one results from the B3LYP calculation with cc-p5TZ basis set. The proton affinity of benzene (Bz), which has been a subject of enormous experimental[4,5] and theoretical studies,[6] is experimentally evaluated as equal to 180.0 kcal/mol,[5g] although its early experimental values range from 178.8[4f] and 183 ± 3 kcal/mol[4g] to 186 kcal/mol.[4h] In other words, comparing the experimental values, PA(Bz) exceeds PA(H_2O) by 13.5 ± 1 kcal/mol. What is then the proton affinity of the benzene−water complex which has recently become a focus of the considerable attention as the classical example of the πH-bonding? Due to the weakness of the πH-bonding of the Bz-H_2O complex, as determined by the binding energy of about 3.0 kcal/mol,[8] it seems that the preferential protonation site might remain on benzene, in such a way that the protonated Bz−H_2O complex would actually be the complex of the benzenium cation BzH^+ with water. And then, a question of interest is whether a proton-transfer resulting in the protonation of water is possible?

The present work is aimed to address these questions which are actually of importance for the following reasons. One of the reasons is that the $[Bz-H_2O]H^+$ complex is the simplest model of the cation−π interaction viewed as a key for molecular recognition in aqueous media[9a−c] and of the transport of ions across the interface of two immiscible phases like, e.g., the water−oil interface.[9d−f] The result of a MP2/6-31G(d,p) calculation carried out recently[9c] predicts its binding energy $E_b = 19.4$ kcal/mol, although the question regarding the energetically preferential protonation site has not been clear so far. The other reason is related to the fact that, experimentally, the protonation of benzene is often performed with the oxonium ion; thus, a theoretical study the interaction of these systems to reveal a possible pathway of proton exchange is of considerable interest.[4,10] On the other hand, such a study also provides some insight into the behavior of protonated aromatic compounds in solvents and shed a light on a rather controversial problem of an existence of the benzenium cation as a face-protonated π-complex.[4−6]

2. Computational Framework

All computations were performed at the second-order Møller−Plessett perturbation theory MP2/6-31+G(d,p) computational level using GAUSSIAN 98 suit of packages[11] with the core orbitals kept frozen. This computational level adequately describes the ground states of benzene of the point group symmetry D_{6h}, water molecule, and their protonated species. Particularly, the calculated C−C and C−H bond lengths are equal to 1.400 and 1.0867 Å, respectively, which is in rather good agreement with the latest experimental findings, 1.3902 ± 0.0002 and 1.0862 ± 0.0015 Å, respectively,[5g] and the high-level MP2(full)/TZ2P+f computational data, 1.3896 and 1.0804 Å, respectively.[12]

The stationary points on the potential energy surface (PES) of the $[Bz-H_2O]H^+$ complex were further distinguished by calculating their harmonic vibrations at the same computational level. The harmonic frequencies and zero-point vibrational energies (ZPVE) were retained unscaled. At this computational level, the eight harmonic stretching vibrations of Bz are calculated at 3249 (B_1 symmetry, 7), 3259 (E_2, 7), 3259 (E_2, 7), 3274 (E_1, 36), 3274 (E_1, 36), and 3284 cm^{-1} (A_1, 7) where the irreducible representation of the D_{6h} point group and the corresponding IR intensity in km/mol are given in parentheses. Throughout the present work, the energy comparison was made in terms of the MP2(fc)/6-31+G(d,p)+ZPVE[MP2(fc)/6-31+G(d,p)] energies. At this computational level, we obtain PA(H_2O) = 164.2 kcal/mol, and PA(Bz) = 174.7 kcal/mol. The binding energy of the Bz−H_2O complex with water at the position Leg1[8b] is equal to 2.9 kcal/mol. The basis set superposition error (BSSE) effect was also accounted for using the known counterpoise procedure.

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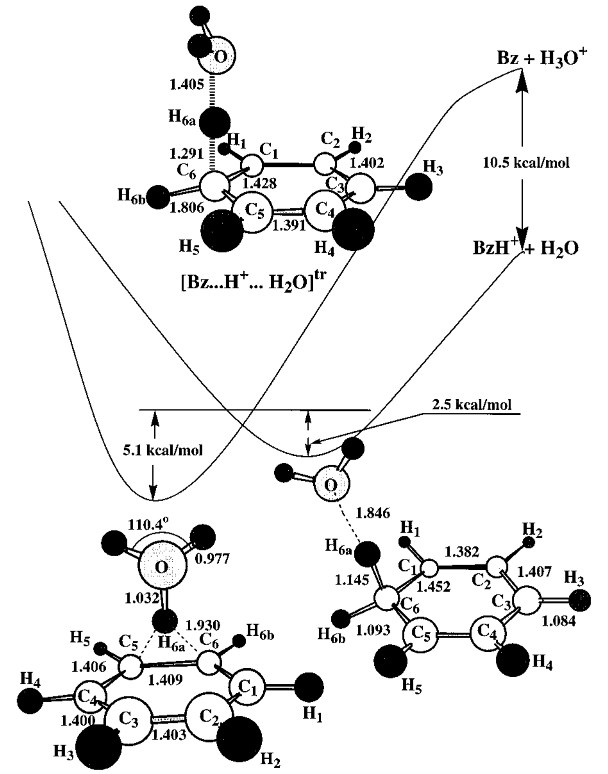

Figure 1. Potential energy profiles along the excess proton reaction coordinate in the protonated benzene−water complex. Bond lengths in angstroms.

TABLE 1: Geometries of the Protonated Bz−H_2O Structures[a]

geometry	BzH^+	Bz−H_2O	Bz−H_3O^+	BzH^+−H_2O	$[Bz\cdots H\cdots H_2O]^{tr}$
$r(C_1C_2)$	1.377	1.400	1.400	1.382	1.391
$r(C_1C_6)$	1.466	1.400	1.406	1.452	1.428
$r(C_2C_3)$	1.410	1.400	1.403	1.407	1.402
$r(C_1H_1)$	1.083	1.083	1.083	1.083	1.083
$r(C_2H_2)$	1.081	1.083	1.083	1.081	1.082
$r(C_3H_3)$	1.085	1.083	1.083	1.084	1.083
$r(C_6H_{6a}$	1.105	1.083	1.084	1.145	1.291
$r(C_6H_{6b}$	1.105			1.093	1.086
$\angle C_1C_2C_3$	119.0	120.0	120.2	119.1	119.7
$\angle C_2C_3C_4$	123.1	120.0	120.2	122.6	121.4
$\angle C_2C_1C_6$	120.8	120.0	119.9	120.2	119.7
$\angle C_1CC_5$	117.4	120.0	119.9	118.1	119.2
$\angle C_6C_1H_1$	118.4	120.0	119.8	118.8	119.4
$\angle C_1C_2H_2$	121.1	120.0	119.9	120.8	120.2
$\angle C_2C_3H_3$	118.5	120.0	119.9	118.7	119.3
$\angle C_1C_6H_{6a}$	109.3	120.0	120.2	101.6	92.7
$\angle C_1C_6H_{6b}$	109.3			115.3	118.6
$\angle H_{6a}C_6H_{6b}$	100.9			100.8	103.0

[a] Bond Lengths in angstroms, bond Angles in degrees. Numbering of atoms is indicated in Figure 1.

3. The Protonated Benzene−Water Complex

We consider the portion of the ground-state PES of the [Bz−H_2O]H^+ complex which possesses two minima corresponding to the Bz−H_3O^+ and BzH^+−H_2O structures with the binding energies of 24.48 and 11.38 kcal/mol, respectively. The BSSE corrected energies are then equal to 23.12 and 10.12 kcal/mol, respectively. These structures are both displayed in Figure 1, and their geometries are collected in Table 1. The former complex resides at the global minimum of the PES being more stable than the latter by 2.62 kcal/mol, and it is actually, to our knowledge, the first reported example of the ionic πH-bonding. It thus implies that, despite the fact that benzene is more basic than water that might be not dramatically changed by forming a rather weak Bz−H_2O complex,[8b] the preferential site of its protonation becomes placed on water and forms the oxonium ion−Bz complex. In the Bz−H_3O^+ complex, the oxonium ion forms a nearly symmetrical bifurcated H-bond of the ionic O−H···C type with two adjacent carbon atoms of benzene. The latter ones move slightly apart from each other by −0.01 Å. As seen in Figure 1, the O−H···C bond length in this case comprises of −1.93 Å, which is quite shorter compared to that in the neutral HOH−Bz complex.[8b] The O−C distance is equal to 2.92 Å. The related bond angle ∠OHC is equal to −158.0°. Upon formation of the O−H···C bond, the O−H distance is elongated by 0.05 Å compared to the O−H bond length in free H_3O^+, whereas the angles to the adjacent O−H bonds are descreased by 1.7°, and in contrast to the Leg1 structure of the Bz−water complex,[8b] its O−H bond is nearly perpendicularly pointed downward to the benzene ring.

Spectroscopically, the formation of the bifurcated ionic πH-bond in the Bz−H_3O^+ complex manifests in redshifting of the stretching vibration of the participated O−H bond from 3620 cm^{-1} of the oxonium ion to 2693 cm^{-1} in the Bz−H_3O^+ complex. Therefore, this redshift which comprises of 927 cm^{-1}, is typical for ionic H-bonds. This stretching vibration is enormously enhanced by a factor of 51. The symmetric ν_1 type stretching vibration of the two other O−H bonds of the oxonium ion is also redshifted by 55 cm^{-1}, whereas their asymmetric stretching vibration shows a similar blue shift.

The benzenium cation−water BzH^+−H_2O complex is formed by the ionic C−H···O bond with the length of ~1.85 Å, the bond angle of 176.3°, and the C−O separation of 2.99 Å (see Figure 1). Its formation is also accompanied by the lengthening of the adjacent C−C bonds by 0.05 Å. By analogy with the Bz−H_3O^+ complex, the C−H bond is elongated by 0.06 Å and its stretching vibration is found at 2549 cm^{-1} being significantly enhanced. The adjacent C−H bond is lengthened by 0.01 Å only and its stretching vibration is observed at 3165 cm^{-1}. The stretching vibrations of water molecule, ν_1 and ν_3, are red shifted by 36 and 51 cm^{-1}, respectively, and become more IR active.

In summary, one finds that the formation of the ionic H-bond in the [Bz-H_2O]H^+ complex affects the geometry of the benzene ring in substantially different ways depending on whether the O−H···C or the O···H−C bond is formed. On the one hand, regarding the former bond, the benzene ring geometry remains almost unchanged. On the other hand, the formation of the O···H−C bond causes noticeable deformations of the benzenium ring. In particular, two neighboring C−C bonds are shrinked by 0.014 Å, accompanied by elongation of the second-neighboring C−C bonds by 0.005 Å, whereas the third one becomes compressed by only ~0.003 Å.

4. Proton Transfer in [Bz-H_2O]H^+ Complex via Avoided Crossing

The preceding section demonstrates that the [Bz−H_2O]H^+ complex has two minimum energy structures with the energy offset of 2.6 kcal/mol connected by a proton transfer. The latter is governed by the transition structure $[Bz\cdots H\cdots H_2O]^{tr}$ shown in Figure 1. Its geometry is given in Table 1. It follows from this table that the migrating C−H bond lies almost perpendicular to the benzene ring whereas its adjacent C−H bond nearly in the molecular plane. The barrier height amounts to about 5.1 kcal/mol, relative to the lower energy complex. It is characterized by the imaginary frequency 507i cm^{-1} describing the stretching of the C−H bond as the reaction one by 0.14 Å and shortening of the related C···H···O distance by 0.3 Å. With respect to the upper minimum BzH^+−H_2O, the barrier height becomes equal to only 2.5 kcal/mol, so implying that the lower-energy well is accessible by proton tunneling. Comparison of the Mulliken charges on the transferred H atom equal to 0.42 and 0.57 for the BzH^+-H_2O and $Bz-H_3O^+$ complexes, respectively, suggests that this transfer is partly accompanied by an electron transfer. It is worth to notice that at the transition structure $[Bz\cdots H\cdots H_2O]^{tr}$, the transferred H atom has Mulliken charge of 0.50, that is, nearly a half of the sum of its Mulliken charges at both energy wells.

The two complexes BzH^+-H_2O and $Bz-H_3O^+$ are characterized by the dissociation energies of ∼11.4 and 24.5 kcal/mol, respectively. The latter value satisfactorily agrees with the similar estimation performed recently[9c] at the MP2/6-31G(d,p) computational level. In other words, the dissociation channel asymptote of the most stable $Bz-H_3O^+$ complex lies higher than that of the less stable BzH^+-H_2O complex by $PA(Bz) - PA(H_2O) = 10.5$ kcal/mol. This results in an avoided crossing of the corresponding PESs determining the transition state $[Bz\cdots H\cdots H_2O]^{tr}$ which governs the low-energy barrier coupled proton−electron transfer (see Figure 1).

5. Concluding Notices

We have shown the theoretical evidence of that the protonation of benzene−water complex possesses some subtle features and it is likely to occur in two stages. At the first stage, the excess proton favors to approach benzene because it is more basic than water and, via the ionic $C-H\cdots O$ bond, forms the benzenium−water complex. The latter undergoes a further transition to the benzene-oxonium complex via a coupled electron−proton transfer through a low-energy transition state which resembles a π-complex (see refs 4 and 10 for the early discussion) and results from an avoided crossing of both potential energy curves depending on the excess proton reaction coordinate. This demonstrates that the ionic πH-bonding $O-H\cdots C$, or in the other words,[9a−c] the π−cation interaction, is stronger than the ionic $C-H\cdots O$ interaction. The backward transfer is also possible by activation of the ionic πH-bond $O-H\cdots C$. The benzene-oxonium complex can be also interpreted, to some extent, as the edge-on π-protonated benzene in water. It is interesting to compare the protonation of the benzene−water complex with that of benzene-ammonia[13] (see also ref 9c). The experimental PA of ammonia is 204 ± 1 kcal/mol,[1d−e,2−3] so it is more basic than benzene, and therefore, the protonation of the benzene−ammonia complex simply goes in a single stage by attaching the excess proton to the ammonia. Experiments would be welcome for revealing such avoided crossing and to stimulate further theoretical studies.

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